High Photoconductive Nanocomposite Film Based on TiO₂ Nanotube Arrays and Copper Phthalocyanine

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Abstract

Size-controllable and vertically oriented TiO₂ nanotube arrays were fabricated using anodic oxidation of pure titanium sheets in electrolyte solutions, and were characterized by field-emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and X-ray diffraction (XRD) patterns. It was found that the dimensions and the ordered morphology of TiO₂ nanotubes could be tuned by altering anodic voltage, oxidation temperature. time and annealing Adouble-layered photoconductive device (Au / copper phthalocyanine (CuPc) / TiO₂ nanotubes /titanium) was designed and fabricated based on the TiO₂ arrays. The I-V curves demonstrated typical heterojunction characteristics and remarkable photoconductive performance with the current value increasing by 1 or 2 orders of magnitude when exposed to light from dark.

Keywords: TiO₂; nanotube arrays; composites; photoconduction

1. Introduction

Fabrication of nanometer-scale components in desired geometries is of significance for the new generation of optoelectronic devices [1,2]. Generally, the performance of the optoelectronic devices based on the donor-acceptor heterojunction could be improved either by increasing the interfacial area between the two construction materials in devices or restricting the transport direction of carriers to make sure of their directional transportation to the electrodes [3]. Vertically-aligned nanostructure arrays with a high surface-to-volume ratio meet both of the requirements perfectly because of their well-defined transportation channels for carriers and tremendous surface area. However, due to the poor solubility in organic solvents and difficulty in forming huge single crystals, organic semiconductors could hardly self-assemble into ordered nanostructures. Templateassistant-synthesis method [4,5] has proved to be a versatile approach for nanomaterials synthesis due to the convenience in controlling the size of the resulting nanostructures. One of the most extensively used templates is the anodic aluminum oxide (AAO) membrane [6].

However, as an inert material in optoelectronic devices, alumina membrane has to be removed after finishing its mission, so that another semiconductor material could be composited with the as-prepared organic nanoarrays, which increases the production cost and reduces the performance of devices. As an excellent inorganic semiconductor, TiO_2 can directly composited with the filling guest materials without the trouble to remove it.

Herein, we report a single junction Au/copper phthalocyanine (CuPc)/Titania nanotubes (TNTs)/Ti device, which behaved 1 or 2 orders of magnitude increasing in current value when exposed to light from dark.

2. Experimental

2.1 Fabrication and characterization of TiO2 nanotube arrays

Titanium foils (thickness 0.3mm and 99.9% pure) were purchased from Hongtai rare metal Inc., Shanghai, China. The other chemicals used in this work were commercially available. The titanium foils were ultrasonically cleaned in scour, deionized water, followed by ultrasonic rinsing in isopropanol, acetone, toluene and alcohol in turn for 10 minutes prior to anodization. The electrolyte consisted of 0.1 M potassium fluoride in 1.0 M sulfuric acid. The anodization was performed in a two-electrode electrochemical bath with a platinum electrode served as the cathode at a constant potential with a DC power supply (TPR-6405D). The foils were anodized using a potential in the range of 10~20 V for 30~360 min for all of the samples in this study. The samples were cleaned using deionized water after completing the anodization process.

All as-prepared TiO₂ samples were annealed at temperatures ranging from 28°C to 600°C in oxygen ambient for 6 h with heating and cooling rates of 2°C/min. The morphologies of samples (surface as well as lateral topography of the nanotubes) and elemental analysis of the TNTs were studied by using a fieldemission scanning electron microscope (FESEM; SIRION, FEI, Netherlands) fitted with an energy dispersive X-ray microanalysis system (EDX). The crystallization and evolution of different phases of TiO₂ nanotube arrays were detected and analyzed by Xray diffraction (XRD) on a D/Max-2550PC diffractometer (Rigaku, Japan). The structure of the nanotube arrays were recorded on a transmission electron microscope (TEM, JEM-1230). The nanotubes were scratched from Ti metal substrate, dispersed in ethanol and then transferred to copper grids for TEM tests.

2.2 Fabrication and characterization of photoconductive devices

CuPc layers with 100 nm thickness were deposited on anodized TiO_2 samples by thermal evaporation with a deposition rate of 1.0 nm/min.

The fabrication of the photoconductive devices were finished by depositing 20~25 nm Au film on CuPc/TNT composites as a semi-transparent electrode. The photocurrent (I) and photovoltage (V) of the devices were measured on Agilent Technologies 4155C Semiconductor Parameter Analyzer under the simulated AM 1.5 solar illumination (100 mW/cm²) produced by a 500-W Solar Simulator (Oriel Corp., USA). All tests were performed in atmosphere.

3. Results and Discussion

3.1 Effect of anodization conditions and annealing temperature on the morphology and structure of TiO₂ nanotube arrays

Fig.1 presents the FESEM images of as-prepared TNT arrays anodized at different potentials. The nanotube pore size was found to be proportional to the applied potential and independent of the anodization time. Increasing the potential from 10 V to 20 V increased the diameter of the resulting nanotubes from 40 nm to 115 nm. No obviously effect of anodization time on the pore size of nanotubes was found.



Figure 1. FESEM images of as-prepared TiO_2 nanotube arrays anodized at (a) 10 V, (b) 15 V, and (c) 20 V, respectively. All scale bars are 500 nm.

As can be seen in Fig. 2, no significant difference was observed in the tube pore size between anodization time of 30 min and 120 min. However, nanotube lengths were increasing with prolonging the anodization time. For example, with the anodization time extending from 30 min to 120 min (at a potential of 15 V), the nanotube length increased from 90 nm to 240 nm (see Fig. 2).



Figure 2. FESEM cross-sectional images of as-prepared TiO_2 nanotube arrays anodized at 15 V for (a) 30 min, (b) 60 min, and (c) 120 min. All scale bars are 500 nm.

Table 1. The effect of anodization conditions on the size of Ti	02
nanotubes.	

Potential (V)	Time (h)	Diameter (nm)	Length (nm)
10	2	40±10	111±30
	6	40±10	105±35
15	2	65±15	231±60
	6	65±15	233±60
20	2	100±20	350±130
	6	100±20	352±130

Table 1 shows the diameter and the length of nanotubes under different anodization conditions. It is found that the last length of nanotubes is independent of the anodization time at one constant potential. That is to say, the nanotubes with desired sizes could be reached by controlling the anodization conditions.

Fig.3 shows the SEM and TEM images of TiO_2 nanotube arrays made at a potential of 15 V, demonstrating the tubular and hollow structure. From the EDX spectrum in Fig.3 (b), in addition to the Au peak arose from the Au thin film deposited on the surface of sample, no elements other than titanium and oxygen can be found. Therefore, it is evident that the nanotube arrays are composed of titanium oxide.



Figure 3. (a) SEM image, (b) EDX spectrum, and (c) TEM image of TiO_2 nanotube arrays anodized at 15 V.

The X-ray diffraction (XRD) patterns of TiO₂ nanotubes annealed at different temperatures up to 600°C are given in Fig.4. The as-prepared nanotubes were found to be amorphous (only reflections from titanium substrate can be seen). The anatase phase appeared at a temperature near 280°C, and maintains this state up to near 480°C. The rutile phase appeared at 480°C, and its ratio increased with increasing the temperature. With increasing the annealing temperature further to 580°C, rutile phase obtained predominance as evident from the higher ratio of rutile (110) peak to anatase (101) peak. No obvious nanotube damnification was observed in the FESEM images of the annealed samples up to 580°C, while collapse and disappearance of the nanotubes could be found when temperature exceeded 600°C. The key processes fundamental to the formation and the phase transformation mechanism of the as-prepared TNT arrays could be referred in other papers [7].



Figure 4. XRD patterns of the TiO₂ nanotube arrays annealed at temperatures ranging from 28 to 600 \degree in air for 6 h.

3.2 Photoconductive property of Au /CuPc / TiO_2/Ti devices

The structure of the as-prepared photoconductive devices (Au /CuPc (100 nm)/TiO₂ (200 nm)/Ti) is schematically given in inset of Fig.5. The diameter of the TiO₂ nanotube arrays is 45 nm here. Fig.5 presents the photocurrent (I) and photovoltage (V) of the devices measured under the AM 1.5 solar illumination (100 mW/cm²). It is seen that both photocurrent and dark current present typical heterojunction characteristics. Besides, the photocurrent is higher than the dark current by 1 or 2 orders of magnitude at the same bias voltage in the range from 0.5 to 1.5 V. For voltage of 1.28 V, the photocurrent is 0.088 mA/cm², about 89.5 times higher than the dark current of 9.8×10^{-4} mA/cm².



Figure 5. I-V characteristics of the devices under AM 1.5 (100 mW/cm^2) illumination, inset is the schematic structure of the device.

Assuming that CuPc (donor) absorbs incident photons and yields excitons, the nanostructure of TNTs (acceptor) enormously increases the contact areas between CuPc and TiO₂ to offer much more sites where the excitons are dissociated. The highest occupied molecular orbital (HOMO) of CuPc and TiO₂ are 5.2eV and 7.4eV, respectively. The barrier energy between them forbids holes running into TiO₂ effectively. The energy difference between the lowest unoccupied molecular orbital (LUMO) of CuPc (3.5eV) and TiO₂ (4.2eV) does the same thing on electrons. The little difference in energy bands of CuPc and TiO₂ with their respective contact electrodes (Au for CuPc, and Ti for TiO₂) are appreciable for charge transfer after photo excitation. Then, the directional and well-ordered structure of TNT arrays can act as efficient transport channels, thus the collection efficiency of electrons are greatly enhanced, leading to an evident increase of photocurrent.

4. Conclusions

In summary, TiO_2 nanotube arrays were prepared in fluoride containing acidic electrolytes at anodization potential from 10 V to 20 V. The nanotubes with desired sizes could be achieved by altering anodization voltage and time, so did the crystallization of nanotubes by regulating annealing temperature of films. Furthermore, an original Au/CuPc/TiO₂/titanium photoconduction device was designed and fabricated. The I-V curves demonstrated that this device showed typical heterojunction characteristics, and the current value changed by 1 or 2 orders of magnitude when the devices switched to light from dark or reversal.

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Author Biography

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